Model Discrimination of Radical Desorption Kinetics in Emulsion Polymerisation

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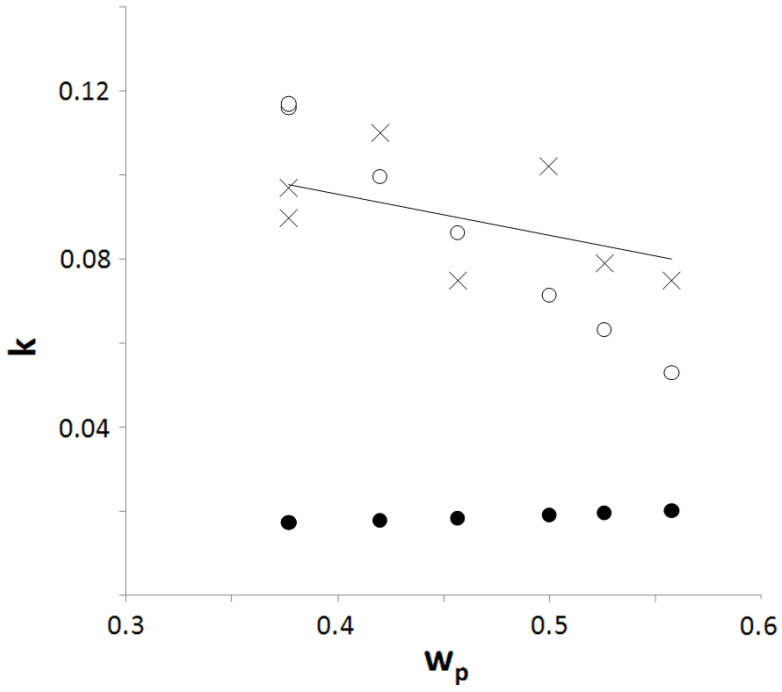
Abstract

Analysis of published experimental data on monomeric radical diffusion in the emulsion polymerisation of styrene shows that it can be quantitatively described equally well by non-equilibrium diffusion from particles, where all parameters are derived from properties of the discrete phase, or by steady-state diffusion where all parameters are derived from properties of the continuous phase. The non-equilibrium model better describes an observed experimental trend to a reduced desorption rate coefficient at higher weight fraction of polymer in the particles. The theoretical upper bound of the non-equilibrium model is also higher than the theoretical upper bound of the steady-state model allowing fits to experimental data which must be discarded as anomalous in the continuous phase model.

Graphic for Abstract



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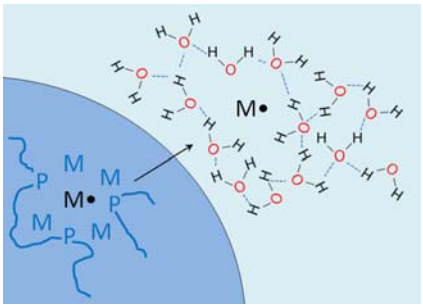
Diffusion of monomeric radicals in emulsion polymerisation can be described by non-equilibrium diffusion from particles controlled by properties of the discrete phase, or by steady-state diffusion controlled by properties of the continuous phase. The non-equilibrium model better describes the trend to a lower desorption rate coefficient as the weight fraction of polymer in the particles increases.

Graphic for Table of Contents



Introduction

The coefficient for desorption of monomeric radicals from polymer particles, k, is one of the key kinetic parameters in emulsion polymerisation; together with the entry coefficient of oligomeric radicals, ρ, it is the prime determinant of the number of radicals per particle, $\bar{n}$, and hence the overall rate of reaction. Under zero-one conditions, where each particle contains either one or zero polymeric radicals, the number of radicals in a particle will be given by the solution of the equations for first-order or second-order exit:

$$\frac{d\bar{n}}{dt} = \rho(1 - 2\bar{n}) - k\bar{n} \qquad (1a)$$

$$\frac{d\bar{n}}{dt} = \rho(1 - 2\bar{n}) - 2k\bar{n}^2 \qquad (1b)$$

The overall rate of monomeric radical exit will depend on the rate at which these radicals are generated by chain transfer to monomer, $k_{tr}[M]_p$, their rate of desorption from the particle, k_{dM}, and the rate at which they undergo their principal alternate fate, addition to monomer, $k_{p1}[M]_p$. The expression relating the observed rate coefficient for exit, k, to these three terms will depend on the ultimate fate of the exiting radical.

Under conditions where exit is second order in $\bar{n}$ – i.e., all exiting radicals eventually re-enter to terminate growing polymer chains – k is given by:

$$k = \frac{k_{tr}k_{dM}}{k_{p1}} \qquad (2)$$

Under conditions where exit is first order in $\bar{n}$ – i.e., all exiting radicals are consumed by some process in the continuous phase – k is given by:

$$k = \frac{k_{\mathrm{tr}}[\mathrm{M}]_{\mathrm{p}}k_{\mathrm{dM}}}{k_{\mathrm{dM}}+[\mathrm{M}]_{\mathrm{p}}k_{\mathrm{p1}}} \qquad (3)$$

While it has been generally accepted that exit is second-order in the emulsion polymerisation of styrene, consistent with the main fate of exited radicals being re-entry and termination,[1, 2] the experimental evidence is primarily for large particles where the difference between first-order and second-order rate coefficients is small[3] and this remains an active area of investigation.[4]

Uncertainty persists in all coefficients appearing in the right hand side of equations 2 and 3, even for so well-studied a monomer as styrene. While values for k_{tr} are consistent, they date to experimental work performed over fifty years ago.[5] The phenomenal improvement in the accuracy of determination of long-chain k_p values achieved through pulsed-initiation polymerisation over recent decades has made relatively little difference to the accuracy with which k_{p1} values are known, but radical trapping experiments suggest that k_p for the initial step of polymerisation is $10k_p$ or greater for most monomers.[6] As the radical generated by chain transfer to monomer is not identical to the monomer generated by addition of an initiating radical to monomer, this can be considered only a rough guide to the k_{p1} value appropriate for radical exit. Finally, k_{dM} cannot yet be determined independently by experiment and can only be estimated by fitting experimental data to equation 2 or 3, or a priori from an assumed model for desorption.

Hernandez and Tauer have recently reviewed a range of models for the estimation of k_{dM} in emulsion polymerisation.[7] These models can be divided into two main classes.

One set of models uses a steady-state approximation to relate the rate of monomeric radical desorption to the rate of monomeric radical adsorption, and calculates the latter with reference to properties of the monomeric radical in the continuous phase.[8] The original derivation of this model outlined by Hansen and Ugelstad considers steady-state conditions to apply to the surface of a growing particle, but the steady-state approximation is more applicable to the continuous phase as a whole, for which $k_{ads}[M\bullet]_W = k_{dM}[M\bullet]_P$ will certainly be valid. Usually, it is assumed that the monomeric radical will have identical diffusion behaviour and solubility to the monomer.

Under conditions such that $qD_p > D_w$, where q is the partition coefficient of the monomer between the discrete and continuous phases, D_p and D_w are the diffusion coefficients for monomer in the discrete phase and the continuous phase respectively, and r is the radius of a monomer-swollen polymer particle, Casey et al. report k_{dM} as given by the expression:[9]

$$k_{dM} = \frac{3D_w}{qr^2} \qquad (4)$$

This model has given a good fit to numerous sets of experimental data and is widely used in the emulsion polymerisation community.[10, 11]

In the other set of models, the rate of monomeric radical desorption is calculated considering the rate of diffusion of monomeric radicals from within the polymer particles to the particle surface, which then presents a semi-empirical barrier E_A to bring the numbers generated from experimental monomer diffusion coefficients into reasonable agreement with experimental k values. In this model, k_{dM} is given by the expression:[7]

$$k_{dM} = \frac{\lambda D_p}{r^2} e^{-E_A/RT} \quad (5)$$

Where λ is a constant derived from the fundamental geometry of the system.

More complex forms of these models have attempted to include events in the surfactant layer surrounding the particles and it has not proven possible to fit all experimental data to a reasonable degree without incorporating additional adjustable parameters.[12, 13]

To date, all publications intepreting the kinetics of monomeric radical desorption have applied either a continuous-phase model or a disperse-phase model, and in most cases reasonable agreement could be obtained with experimental data given the degree of elasticity available in the input parameters. No quantitative attempt to discriminate between the two models using the same data set has yet been made to the authors' knowledge.

As can be seen from equations 4 and 5, both models predict an inverse dependence on particle radius, so the appearance of this feature in experimental data cannot be used for model discrimination. This r^{-2} dependence is well attested experimentally.[3]

However, the models predict different behaviour with variation in the monomer content of the growing polymer particles. In the continuous phase model, the experimentally observed reduction in q with decreasing $[M]_p$[14-16] predicts that k_{dM} should increase with increasing weight fraction of polymer, w_p.[2] In the discrete phase model, the strong dependence of D_p on w_p[17] predicts that k_{dM} should decrease with increasing w_p.

In this communication the collection of first-order and second-order exit rate coefficient data for polystyrene at 50°C presented by Morrison et al. in their 1994 paper 'Free Radical Exit in Emulsion Polymerization. II.

Model Discrimination via Experiment' will be examined for w_p dependence and compared with the predictions of the two models briefly outlined above.[2] The statistical significance of any dependence will be assessed and the implications for exit of monomeric radicals in emulsion polymerisation discussed.

Results and Discussion

The second-order and first-order rate coefficients quoted by Morrison et al. for a range of polystyrene experiments of differing r and w_p were fit to the continuous and discrete models as outlined above (equations (4) and (5)), using the following parameters:

$D_w = 1.5 \times 10^{-9}\ m^2 \cdot s^{-2}$

$q = [M]_p/[M]_w$

$$[M]_w = \frac{d_p\left(w_p^{-1}-1\right)}{M_0+\frac{M_o}{d_m}d_p\left(w_p^{-1}-1\right)}\ mol \cdot L^{-1}$$ [18]

$d_p = 1.044\ kg \cdot L^{-1}$ (density of polymer)

$d_m = 0.8788\ kg \cdot L^{-1}$ (density of monomer)

$M_0 = 0.104\ kg \cdot mol^{-1}$

$$[M]_w = \left(\frac{[M]_{p,sat}}{[M]_p}\right)^{0.6} \times [M]_{w,sat}$$ [15]1

$$ln([M]_{w,sat}) = -1.514 - \frac{1259}{T}\ mol \cdot L^{-1}$$ [19]

$[M]_{p,sat} = 6.0\ mol \cdot L^{-1}$

$D_p = 3.188 \times 10^{-9} - 5.607 \times 10^{-9} w_p + 4.078 \times 10^{-10} w_p^{\ 2} + 2.096 \times 10^{-9} w_p^{\ 3}\ m^2 \cdot s^{-1}$[17]

$\lambda = 15$[7] This assumes the average distance a particle located a distance x from the centre of a particle of radius r must diffuse to the surface is $(r^2 - x^2)^{1/2}$.

$k_{p1} = 12.3\ k_p = 3200\ L \cdot mol^{-1} \cdot s^{-1}$ (50°C; $E_A = 32500\ kJ \cdot mol^{-1}$) [20, 21]

[1] Where $[M]_{p,sat}$ and $[M]_{w,sat}$ are the saturated concentrations of monomer in the polymer and aqueous phases, respectively.

$k_{tr} = 3.5 \times 10^{-5}\ k_p$ (50 °C; $E_A = 55900$ kJ · mol^{-1}) [5]

$e^{E_A/RT}$ was treated as an adjustable parameter in the discrete phase model. No adjustable parameters were used in the continuous phase model.

Figure 1 shows theoretical predictions from the continuous ($k_{continous}$) and discrete phase ($k_{discrete}$) models as functions of the experimental (k_{exp}) values for all values of the second-order and first-order exit rate coefficients reported by Morrison et al. for styrene polymerisation at 50°C. To provide the optimal match of the discrete model to this global data set, $e^{E_A/RT}$ was set to 840 for the second-order data, corresponding to an activation energy for transfer of monomeric radical to the aqueous phase of 18.1 kJ · mol^{-1}, and to 1350 for the first-order data, corresponding to an activation energy for transfer of monomeric radical to the aqueous phase of 19.4 kJ · mol^{-1}.

[Figure 1]

Both models show a reasonable correlation between predicted and experimental values for both second-order and first-order rate coefficients. The goodness of fit is clearly superior for the second-order k_{exp} values. While both models are indistinguishably effective in correlating the first-order k_{exp} values, the discrete-phase model more closely fits the second-order k_{exp} values. (However, this model contains an adjustable parameter while the continuous-phase model does not.)

Using the values of $k_{tr} = 9.3 \times 10^{-3}$ L · mol^{-1} · s^{-1} and $k_{p1} = 1 \times 10^{3}$ L · mol^{-1} · s^{-1} quoted by Morrison et al. shifts the theoretical curve for the continuous phase model closer to the second-order experimental values (Figure 2). However, there does not appear to be any independent experimental or theoretical justification for assuming such a low value of k_{p1}.[6]

In Figure 2, the data presented by Morrison et al. for all Interval III experiments initiated by gamma radiation is binned according to radius and the experimental and theoretical values of k are plotted as functions of w_p.

[Figure 2]

For each level of particle size and for each estimate of desorption rate, the following regression equation was fitted in an attempt to quantify the goodness-of-fit of the discrete and continuous models to the experimental data of Morrison et al.[22]

$$k = \beta_0 + \beta_1\left(w_p - \overline{w_p}\right) + \varepsilon, \varepsilon \sim N(0, \sigma^2) \qquad (6)$$

Where β_0 is k at mean w_p, the slope of the plot of k vs. w_p is β_1, and ε is the increment by which an individual k may fall off the regression line. ε is assumed to be a normally distributed random variable with mean 0 and variance σ^2.

The model was centred about mean w_p so that slopes could be compared independently of the intercepts.

Figure 3 displays the 95% confidence intervals of slopes for the joint estimates of desorption rate coefficient at mean w_p (β_0) and slope (β_1) for k_{exp}, $k_{continuous}$, and $k_{discrete}$ across categories of particle size for both second-order and first-order k_{exp}. For the second-order k_{exp} values the 95% confidence intervals of β_1 for $k_{continuous}$ overlap the 95% confidence interval of k_{exp} in all cases, while the 95% confidence intervals of β_1 for $k_{discrete}$ and k_{exp} overlap only for the 92-94 nm particles. Thus it appears that the continuous phase model provides a quantitatively better fit to the experimentally observed w_p dependence in the data of Morrison et al. than the simple discrete phase model presented. On the other hand the confidence regions for k_{exp} and $k_{continuous}$ overlap in the X-direction for particle sizes 79-81, 44-45 and 25-26 nm, indicating that the mean desorption rate coefficients were similar across particle size categories. This suggests that the discrete phase model provides a quantitatively better fit than the continuous phase model using physically reasonable k_{p1} values presented. For the first-order k_{exp} values the 95% confidence intervals of β_1 for k_{exp} overlaps the 95% confidence interval of $k_{continuous}$ in all cases but the 92-94 nm particles and the 95% confidence interval of $k_{discrete}$ in all cases but the 44-45 nm particles.

The relative distance between the centres of the confidence ellipses are given in Table 1, below, with the distance between k_{exp} and $k_{continuous}$ set to 1. This suggests there is no quantitative difference in the goodness of fit of the two models to the experimental w_p dependence of k_{exp}.

[Table 1]

[Figure 3]

Although it is desirable to avoid adding adjustable parameters to the models, a weaker dependence on w_p in the discrete-phase model could be achieved non-arbitrarily by making physically reasonable changes to $D_p(w_p)$. The D_p expression used is derived from measurements of bulk polymer samples, but diffusion rates in polymer domains of dimensions of order 20 nm are likely to be higher and less w_p dependent, viz. the observed reduction in glass transition temperatures in thin polymer films in comparison to bulk polymers.[23]

A further possible complication that would tend to reduce the value of $k_{discrete}$ for larger particles relative to smaller ones is the possibility of re-entry. If there is little or no barrier to re-entry of a monomeric radical, then in the absence of any reaction such a radical will have a probability of re-entering the same particle between 0 (if the particle is small enough compared to the radical that it is a point) and 0.5 (if the particle is large enough compared to the particle that it appears to be a plane); thus, there should be a greater probability for re-entry without reaction for large particles than small ones. If there is a significant barrier to re-entry then re-entry to the same particle can be ignored.

While additional barriers to exit may be postulated in the continuous phase model, equation (4) gives a theoretical upper limit to k. Experimental exit rate coefficients have been reported above this theoretical upper limit of the continuous phase model (e.g., [12]). The theoretical upper limit of equation (5), where $e^{E_A/RT} = 1$, will be a significantly larger number. While the complexity of emulsion polymerisation systems means it is always plausible to dismiss an anomalous result as artifactual, it is instructive to compare the prediction of the discrete model as optimised above for the data of Morrison et al. to the anomalous experimental data reported by Thickett and Gilbert (Table 2).

[Table 2]

It can be seen that the discrete-phase model can model the observed results in experiment S0, which has a k_{exp} value above the upper limit of the continuous phase model, and the results of the other experiments can be fit by assuming relatively small and reasonable changes to E_A; there is no need to postulate a very low rate of diffusion ($D = 2.4 \times 10^{-11}\ m^2 \cdot s^{-1}$) through a surface layer of polymeric surfactant.[12]

The values of E_A required to optimise the fit of the discrete model to the Morrison et al. data, 18.1 kJ · mol^{-1} (2^{nd} order) and 19.4 (1^{st} order), are consistent with the values of E_A for desorption of monomeric radicals from polystyrene estimated by Hernandez and Tauer from the work of Casey et al.[9] and Asua et al.,[24] which range from 22.9 to 27.0 kJ · mol^{-1}.[7] These values are comparable to typical free energies of micellisation of 15 to 30 kJ · mol^{-1}[25] and suggest a physical interpretation of the energetic barrier at the surface as the energy required to disrupt the existing water structure and form a solvent cage of low-entropy water around the monomeric radical. This barrier would be unrelated to diffusion, consistent with experimental evidence for the diffusion of styrene showing it to have very similar behaviour in water and in swollen polymer particles.[22,23] As small amounts of hydrogen-bonding or ionic solutes can have dramatic structuring effects on water and the concentration of these species will be locally very high on the surfaces of particles in emulsion polymerisation, variation in E_A with surfactant is to be expected and could be explored by studying the solubility of styrene in bulk solutions of species analogous to surfactants.

The existence of an activation barrier at the surface should be reflected in the variation in k with temperature. The theoretical temperature dependence of each of the models was calculated using reported values for exponential Arrhenius factors. The activation energy for the chain transfer coefficient in styrene, $E_{tr} - E_p$ has been reported by Tobolsky and Offenbach to be 23.4 kJ · mol^{-1}.[26] If $E_p = E_{p1}$, it will follow that the Tobolsky and Offenbach value also equals $E_{tr} - E_{p1}$. The work of Heuts et al. justifies $E_p = E_{p1}$ as it explains the chain-length-dependence of k_p as an entirely entropic rather than enthalpic effect,[27] a result which has been upheld in subsequent work.[6]

In the continuous-phase model it is necessary also to include the temperature dependence of the diffusion coefficient of a monomeric radical in water, E_{D_w}, and of the partition coefficient, E_q.

E_{D_w} may be estimated using the Smoluchowski equation and published values for the viscosity of water as 17.1 kJ · mol^{-1}.

Partition into the polymer phase is expected to be less favourable at higher temperatures. From the data of van Berkel on MMA,[28] E_q may be estimated as –7.5 kJ · mol^{-1}, while combining the expression of Lane for

$[M]_{w,sat}$ of styrene[19] with the empirical relationship of Ballard et al.[15] for the relationship between $[M]_{w,sat}$ and $[M]_{p,sat}$ to give E_q as –8.0 kJ · mol^{-1}.

E_k(continuous) is then $E_{tr} - E_{p1} + E_{D_w} - E_q$, or 48.6-49.0 kJ · mol^{-1}.

In the discrete-phase model, the temperature-dependence of D_p must be estimated. This will be wp dependent and can be estimated to a first approximation by using the data of Blum and Pickup for diffusion of toluene in polystyrene (Table 3).[29] In interval II, this data suggests that E_{D_p} should be 13-14 kJ · mol^{-1}.

[Table 3]

The range of E_A values obtained from experimental data for styrene by fitting the discrete-phase model in this work and by Tauer and Hernandez is 18.1-27.0 kJ · mol^{-1}.[7]

E_k(discrete) is then $E_{tr} - E_{p1} + E_A + E_{D_p}$ or 54.5-64.4 kJ · mol^{-1}.

The only experimental values for E_k to the authors' knowledge are the data obtained by Lansdowne et al., who reported E_k = 42±10 kJ · mol^{-1}.[30] These values were obtained fitting the emulsion polymerisation of styrene in Interval II to a first-order exit model and appear to be more consistent with the continuous-phase than the discrete-phase values calculated above.

From the data presented in Figure 3 of Lansdowne et al., curves of $\bar{n}$ vs. time were generated and fitted to both first-order and second-order exit using the earlier parts of the curves where the contribution of radical entry is minimal. Treatment of a representative data set is given in Figure 4 and the *k* values obtained are given below (Table 4).

[Figure 4]

[Table 4]

The close agreement between the first-order *k* values obtained by the slope and intercept method for the data that were best fit by this method (T = 60, 55, 50) and the first-order *k* values obtained by curve-fitting can be considered a validation of the reprocessing.

Between T = 45 and 65 °C, the temperature range where Lansdowne calculated E_k on the basis that secondary nucleation could be discounted, the recalculated k data gave E_k of 50 kJ · mol^{-1} (first order) and 65 kJ · mol^{-1} (second order). The original first-order estimates and the recalculated first-order estimates are both in reasonable agreement with the prediction of 49 kJ · mol^{-1} of the continuous-phase model. (Recall, however, that the physical assumptions of this model cannot hold in the absence of re-entry.)

The experimental second-order E_k value, on the other hand, is very close to the range of E_k values predicted by the discrete-phase model of 55-64 kJ · mol^{-1}.

Overall the experimentally reported variation in k with temperature is thus not inconsistent with either the continuous-phase or discrete-phase models, though the discrete-phase model appears to be more consistent with the second-order limit, and the physical significance of the continuous-phase model with first-order loss is unclear.

Conclusions

A similar degree of quantitative agreement with published experimental data for exit rate coefficients in the emulsion polymerisation of polystyrene was found using a model for monomeric radical diffusion where all parameters are derived from properties in the discrete phase, with a single adjustable parameter, and a steady-state model where parameters are derived from properties in the continuous phase. The physical interpretation of the adjustable parameter used in the discrete-phase model is straightforward and this parameter is in principle amenable to experimental determination.

The simple discrete-phase model qualitatively reproduces the experimental variation in both second-order and first-order exit rate coefficient k with increasing weight percent of polymer w_p at a constant swollen particle radius r_S, while the continuous-phase model does not, but quantitatively the overall w_p dependence of experimental k is within the 95% confidence interval for the continuous phase model but not the simple discrete-phase model. The theoretical upper bound of the discrete phase model is higher than the upper bound of the continuous phase and in at least one instance can provide a good fit to experimental data which must be discarded as anomalous in the continuous-phase model. The reported effects of a poly(acrylic acid) surfactant layer attributed to a very low rate of diffusion through this layer ($D = 2.4 \times 10^{-11}$ m^2 · s^{-1})[12] may

be modelled equally well by assuming a small increase in E_A due to the water-structuring effect of poly(acrylic acid) as a hydrogen-bonding solute. Finally, experimental estimates for the second-order *k* based on the work of Lansdowne et al. [30] are consistent with the temperature-dependence of *k* predicted by the discrete-phase model and not the continuous-phase model.

Overall the discrete-phase model with one adjustable parameter appears to provide a better fit to the experimental data on radical exit in the emulsion polymerisation of styrene than the continuous-phase model with no adjustable parameters. Additional experimental work to determine exit rate coefficents in Interval III for styrene and other monomers over a range of particle sizes would be of great value in discriminating between the continuous-phase and discrete-phase models.

Keywords

emulsion polymerization, kinetics (polym.)

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Table 1: Relative distance $k_{exp} - k_{discrete}$ from Figure 4, k_{exp} - $k_{continuous}$ = 1

Table 2. Second-order exit rate coefficients for polystyrene at 50°C with varying amounts of polymeric surfactant reported by Thickett and Gilbert.[12]

Table 3: Data of Blum and Pickup for diffusion of toluene in polystyrene.[29]

Table 4: Rate coefficients for exit reported by Lansdowne et al. and recalculated from the data of Lansdowne et al.[30]

Figure 1: Theoretical predictions from the continuous ($k_{continous}$) and discrete phase ($k_{discrete}$) models as functions of the experimental (k_{exp}) values for all values of the second-order and first-order exit rate coefficients reported by Morrison et al. for styrene polymerisation at 50°C.[2] Open circles, $k_{discrete}$; closed circles, $k_{continuous}$. (a) 2nd order k_{exp} with $e^{E_A/RT}$ = 840; (b) 1st order k_{exp} with $e^{E_A/RT}$ = 1350.

Figure 2: Experimental[2] and theoretical values of k plotted as functions of w_p. Open circles, $k_{discrete}$; closed circles, $k_{continuous}$; × = k_{exp}. (a) Second-order k with $e^{E_A/RT}$ = 840; (b) First-order with $e^{E_A/RT}$ = 1350.

Figure 3. Comparison of the estimates of slopes along with their 95% confidence limits for each measurement of desorption rate against w_p for each category of particle size. (a) Second-order k values; (b) first-order k values.

Figure 4: (a) $\bar{n}$ as a function of time at 60°C, recalculated from data in Figure 3 of Lansdowne et al.[30] (b) First-order fit to relaxation data; (c) Second-order fit to relaxation data.

Table 1

	25-26 nm	44-45 nm	79-81 nm	92-94 nm	Average
Second-order k_{exp}	0.53	0.66	0.63	2.16	0.99
First-order k_{exp}	1.30	1.07	0.51	1.52	1.10

Table 2

Sample	r_S (nm)	k_{exp} (10^{-2} L · mol^{-1} · s^{-1})	$k_{continuous}$ ($k_{p1} = 12.3k_p$) (10^{-2} L · mol^{-1} · s^{-1})	$k_{continuous}$ ($k_{p1} = 4k_p$) (10^{-2} L · mol^{-1} · s^{-1})	$k_{discrete}$ (10^{-2} L · mol^{-1} · s^{-1})	Fitted E_A (kJ · mol^{-1})
S0	38.7	3.9	0.81	1.7	6.2	21.8
S5	21.6	1.2	2.6	4.3	1.6	27.1
S10	21.8	0.50	2.6	4.3	0.67	30.5
S20	21.4	0.47	2.5	4.3	0.63	30.6

Table 3

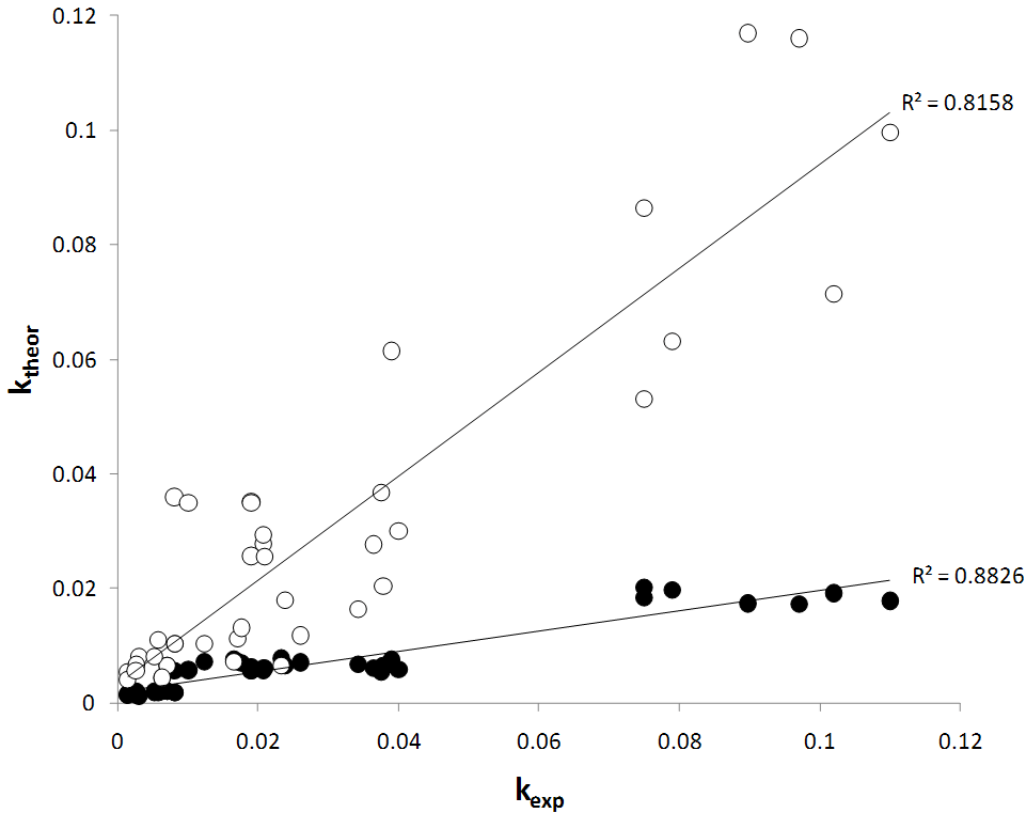
w_p	E_{D_p} ($kJ \cdot mol^{-1}$)
0.201	12.1
0.267	12.5
0.369	13.9
0.444	15.1
0.486	15.8
0.58	18.9
0.603	19.9
0.661	23.1
0.714	26.8
0.791	27.6

Table 4

T	k (first-order1980) $\times 10^{-3}$	k (first-order 2011) $\times 10^{-3}$	k (second-order 2011) $\times 10^{-3}$
65	2.2	1.7	2.8
60	1.6	1.3	2.0
55	1.3	1.1	0.95
50	1.1	1.2	0.95
45	0.82	0.45	0.65
40	0.67	0.27	0.70
30	0.51	0.15	0.45

Figure 1

(a)


0.12
0.1
0.08
0.06
0.04
0.02
0
k_{theor}
0
0.02
0.04
0.06
0.08
0.1
0.12
k_{exp}
$R^2 = 0.8158$
$R^2 = 0.8826$

(b)

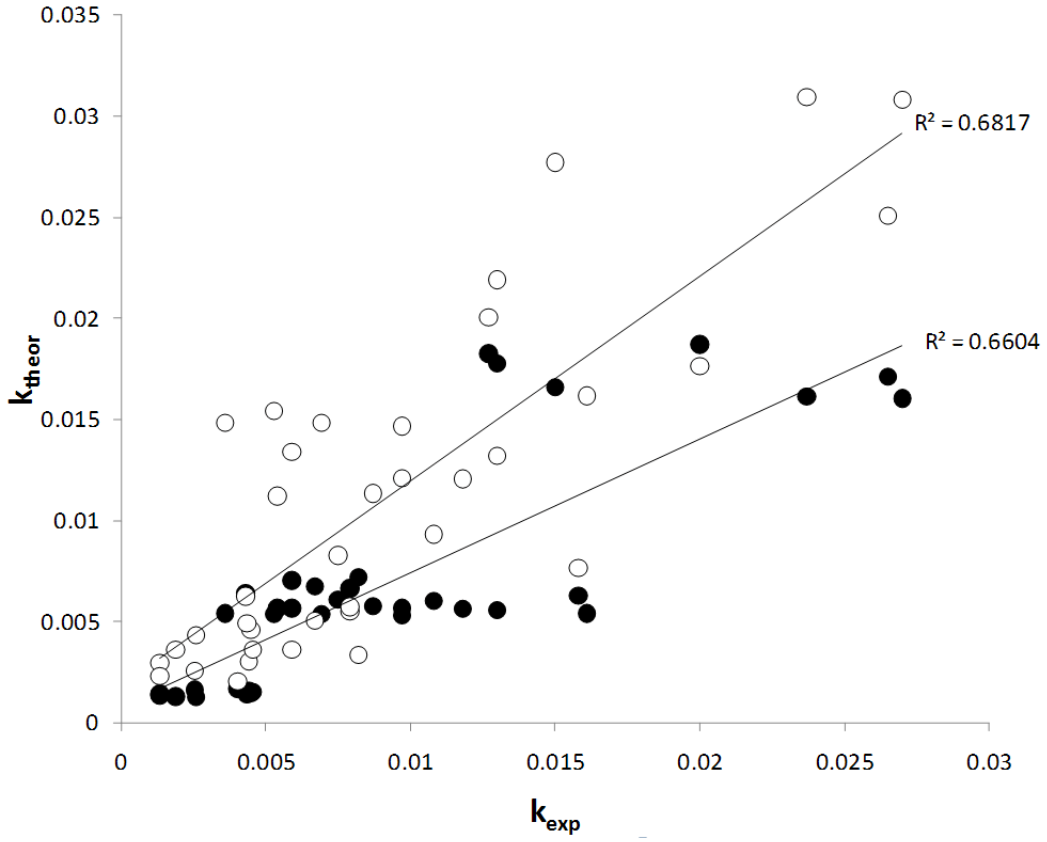
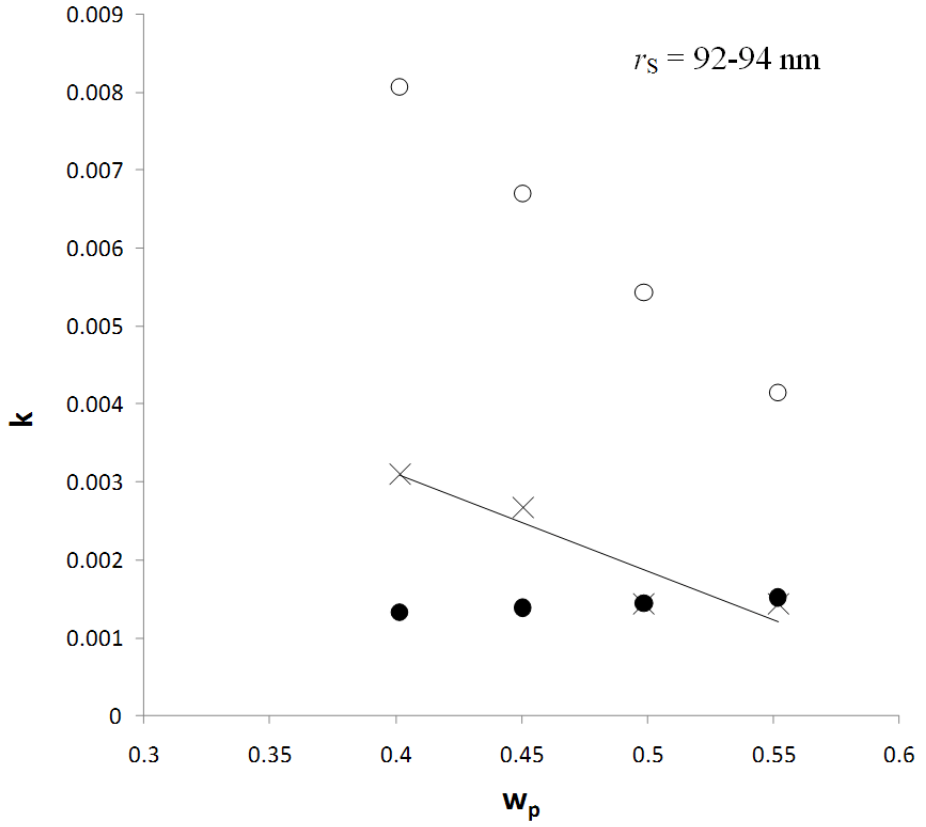
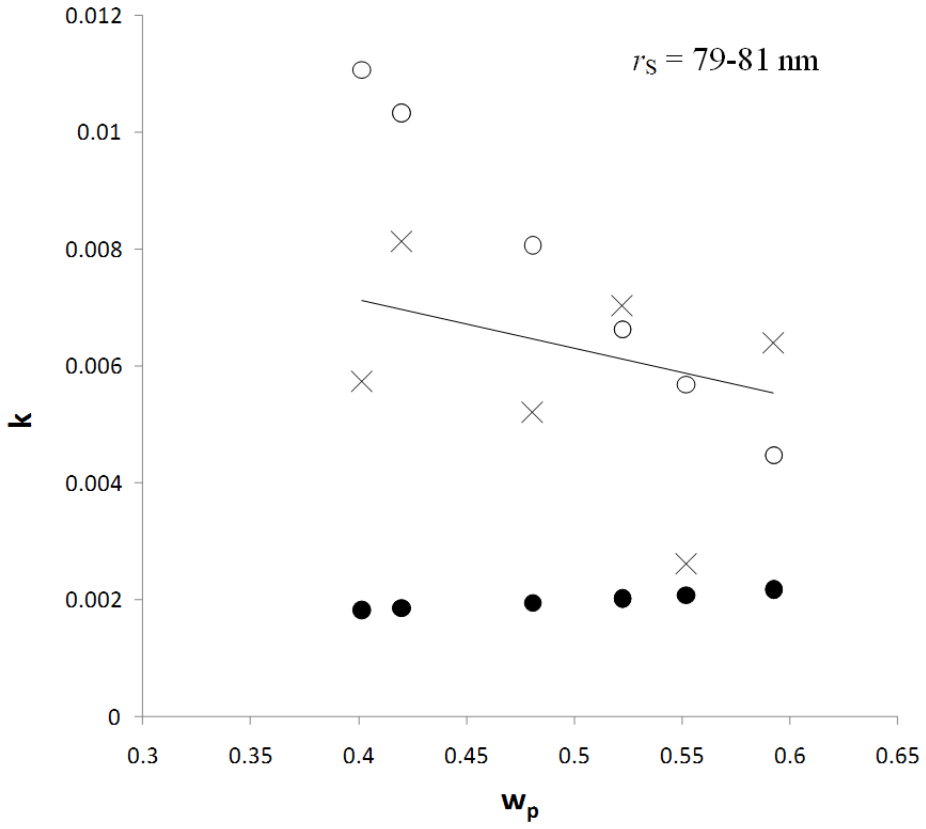
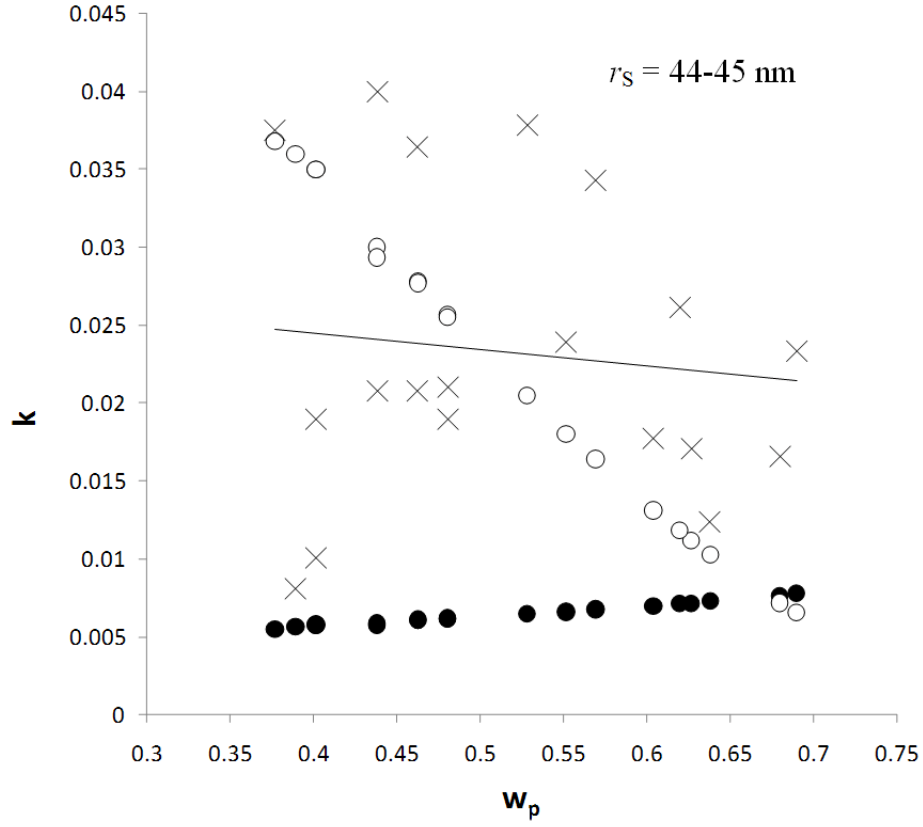

0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
k_{theor}
0
0.005
0.01
0.015
0.02
0.025
0.03
k_{exp}
$R^2 = 0.6817$
$R^2 = 0.6604$

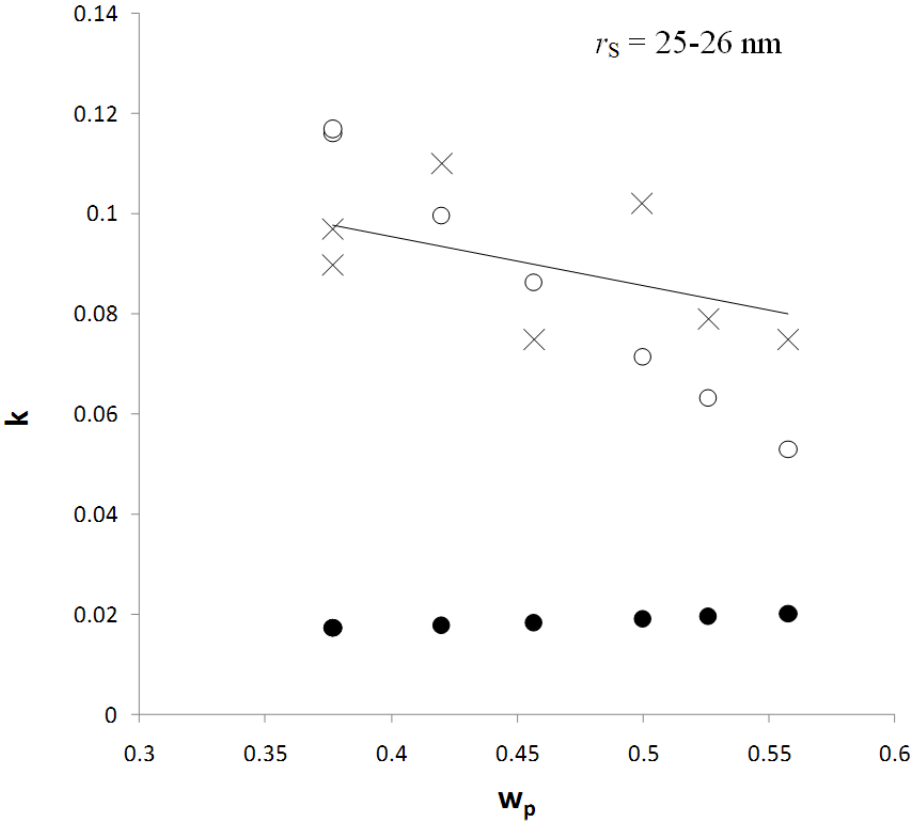
Figure 2

(a)

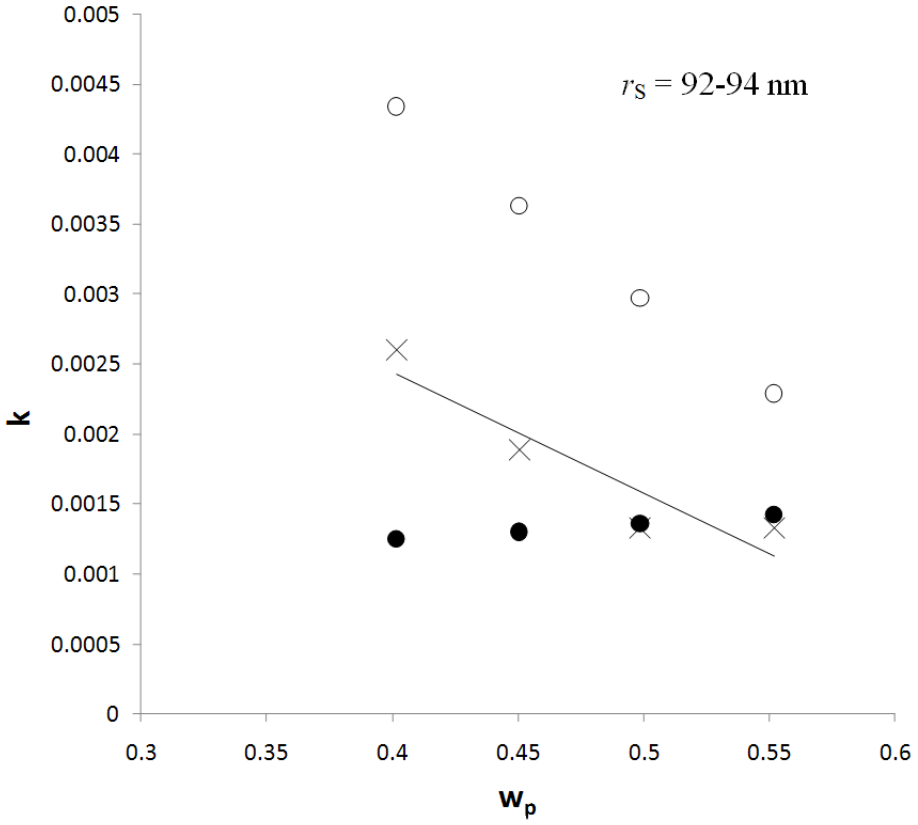

r_S = 92-94 nm
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
k
0.3
0.35
0.4
0.45
0.5
0.55
0.6
w_p

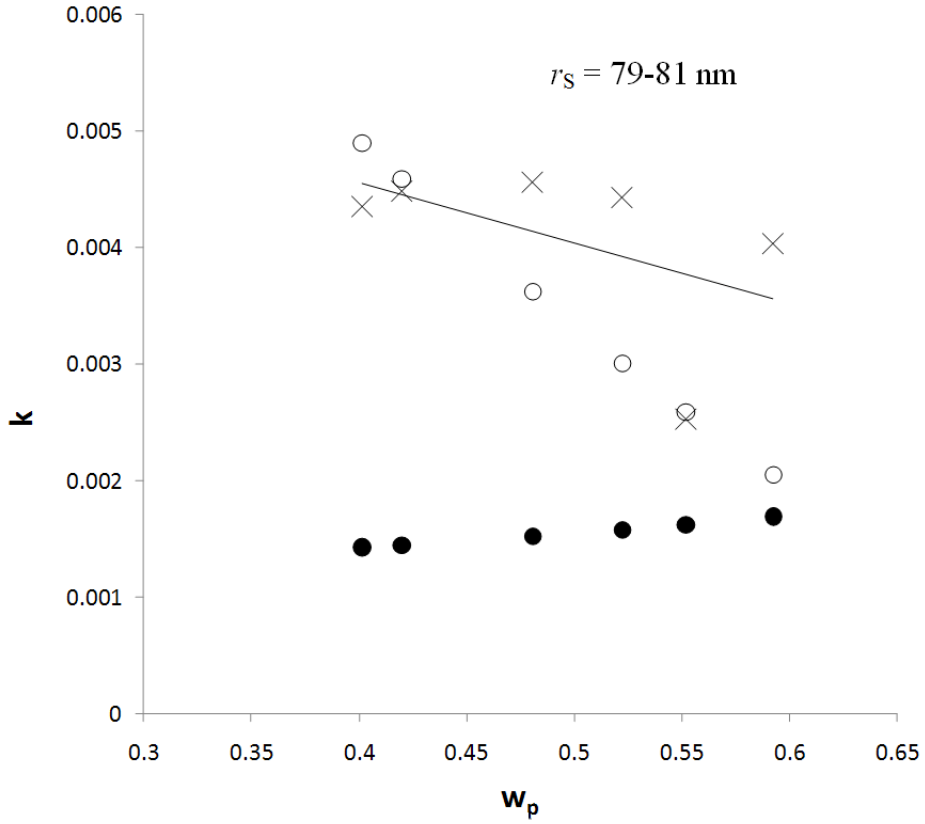

r_S = 79-81 nm
0.012
0.01
0.008
0.006
0.004
0.002
0
k
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65
w_p

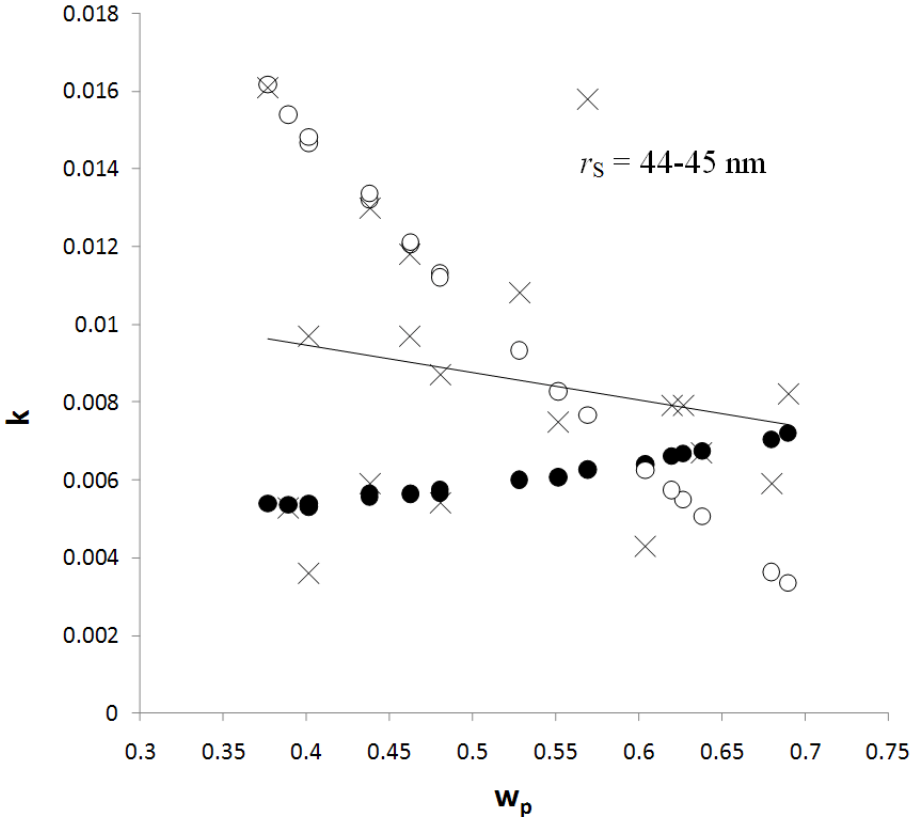

r_S = 44-45 nm
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
k
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65
0.7
0.75
w_p


r_S = 25-26 nm
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
k
0.3
0.35
0.4
0.45
0.5
0.55
0.6
w_p

(b)


r_S = 92-94 nm
k
w_p
0.005
0.0045
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0.3
0.35
0.4
0.45
0.5
0.55
0.6


r_S = 79-81 nm
k
w_p
0.006
0.005
0.004
0.003
0.002
0.001
0
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65


r_S = 44-45 nm
k
w_p
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65
0.7
0.75

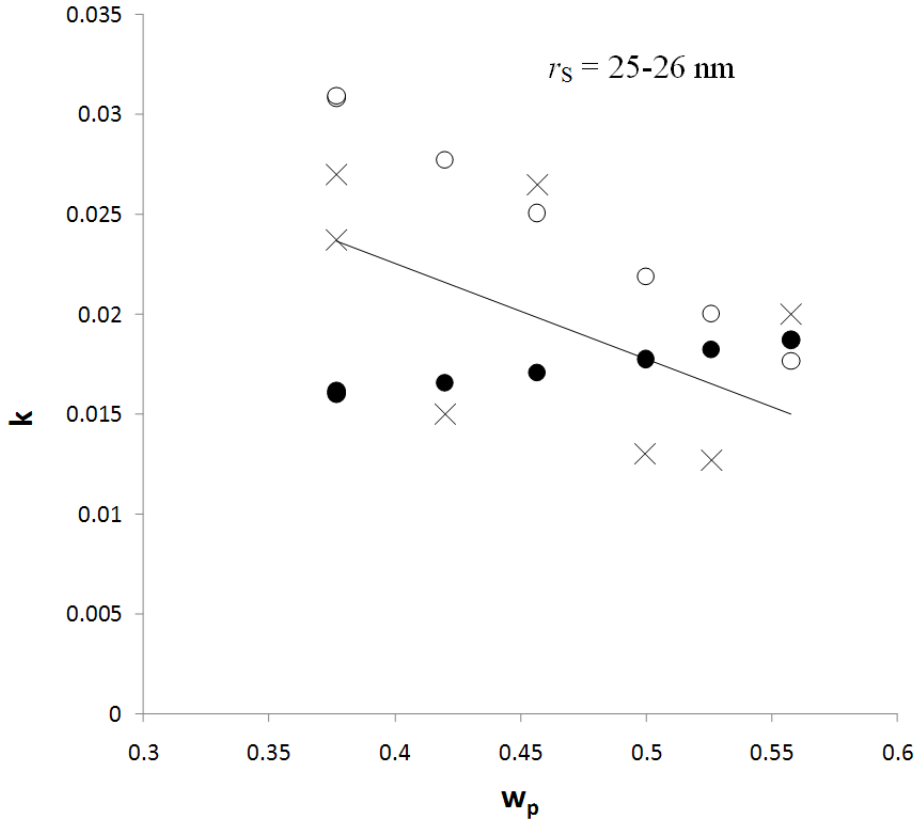
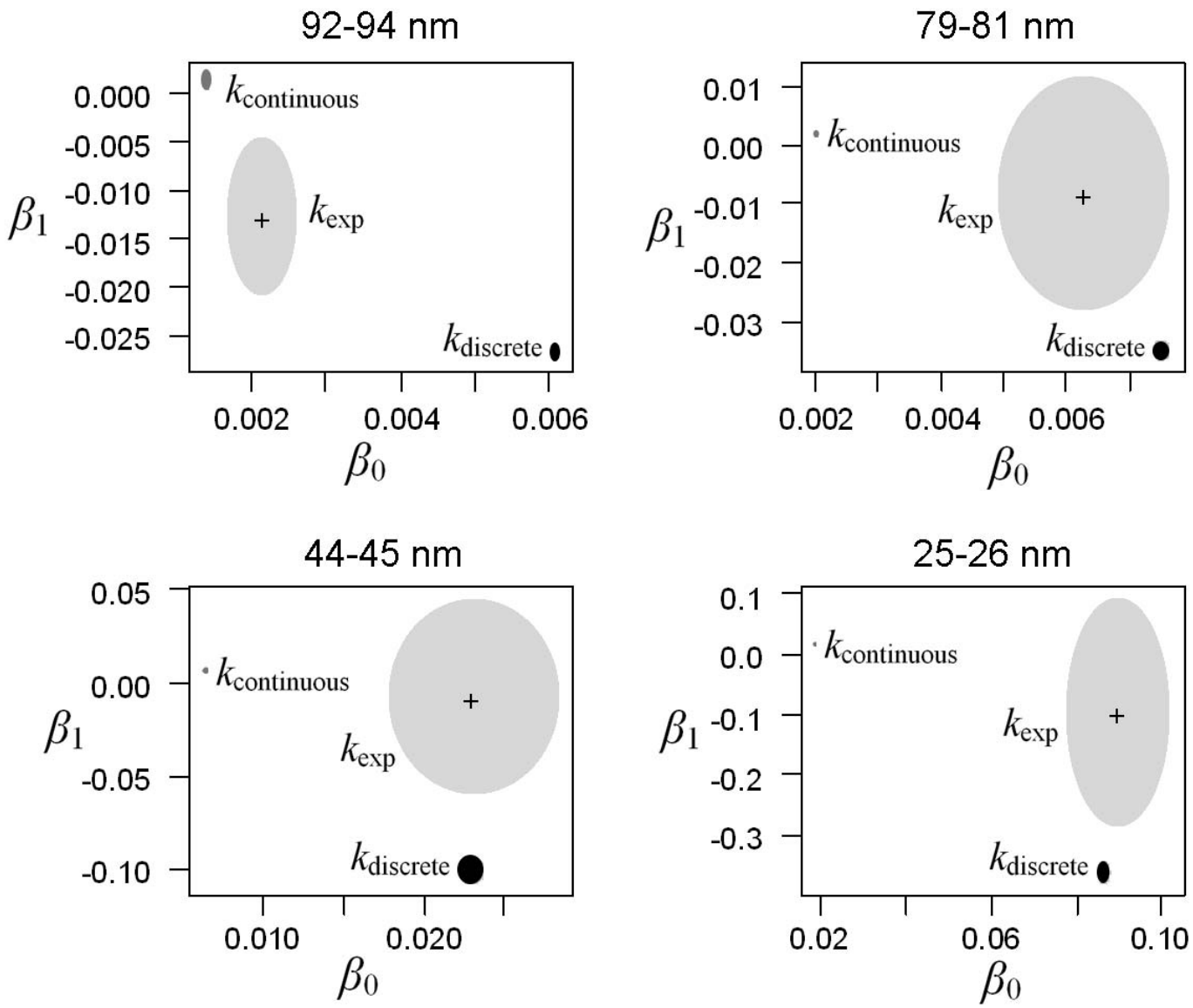

r_S = 25-26 nm
k
w_p
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0.3
0.35
0.4
0.45
0.5
0.55
0.6

Figure 3

(a)


92-94 nm
79-81 nm
44-45 nm
25-26 nm
$k_{continuous}$
k_{exp}
$k_{discrete}$
β_0
β_1
0.000
-0.005
-0.010
-0.015
-0.020
-0.025
0.01
0.00
-0.01
-0.02
-0.03
0.05
0.00
-0.05
-0.10
0.1
0.0
-0.1
-0.2
-0.3
0.002
0.004
0.006
0.010
0.020
0.02
0.06
0.10

(b)

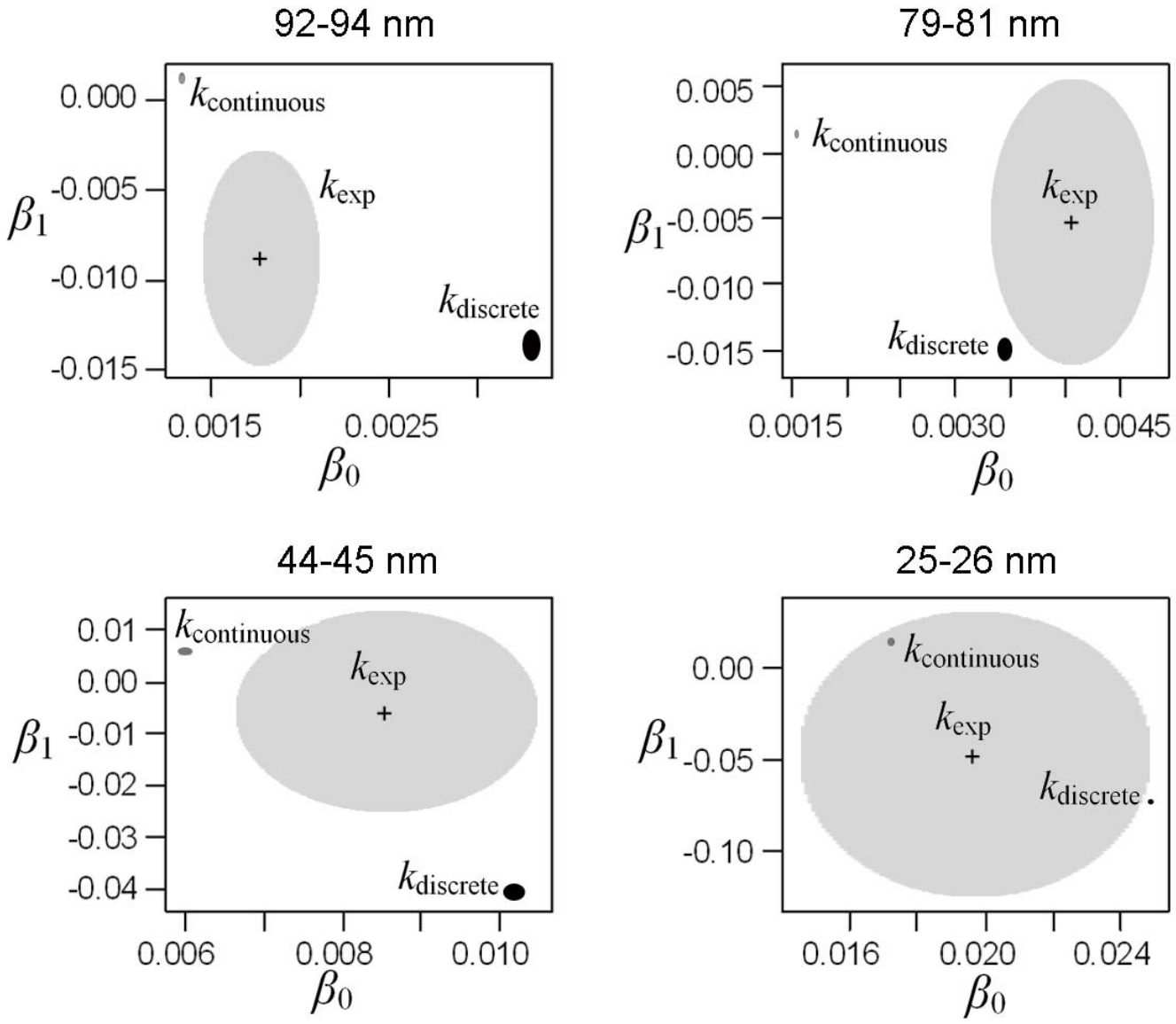
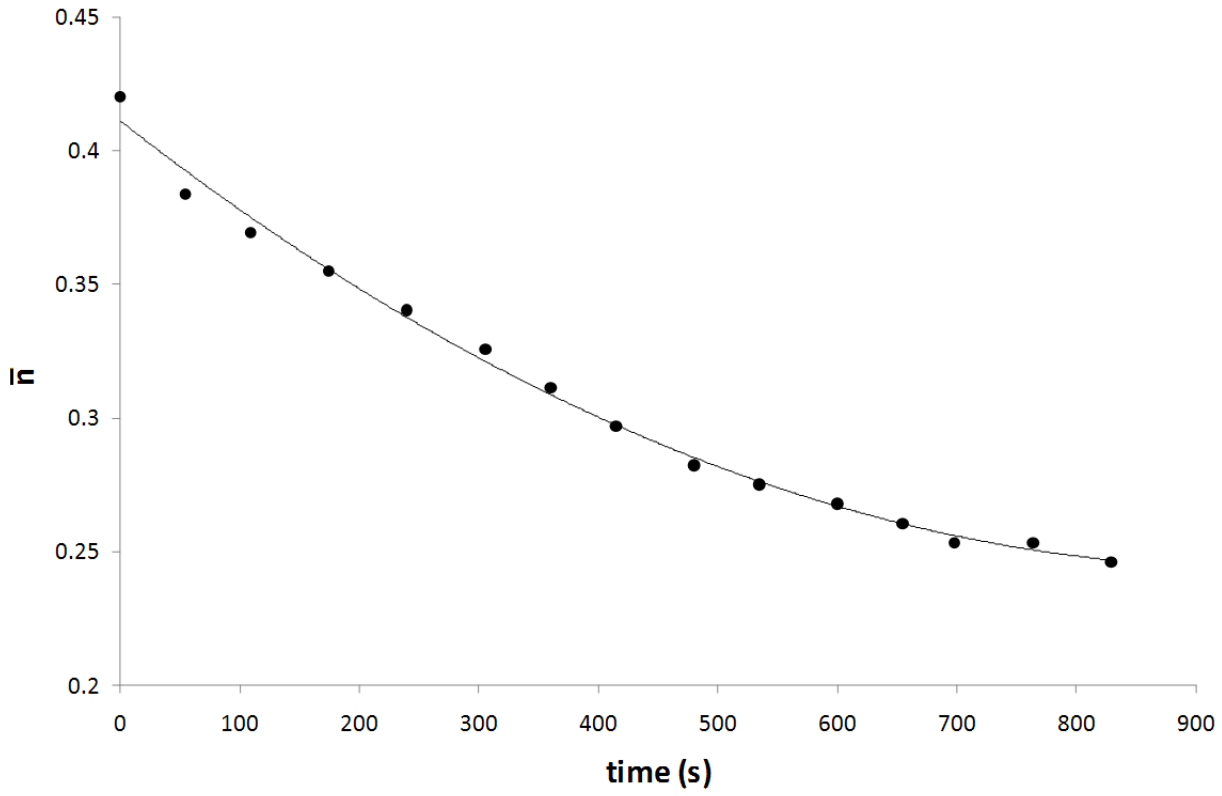
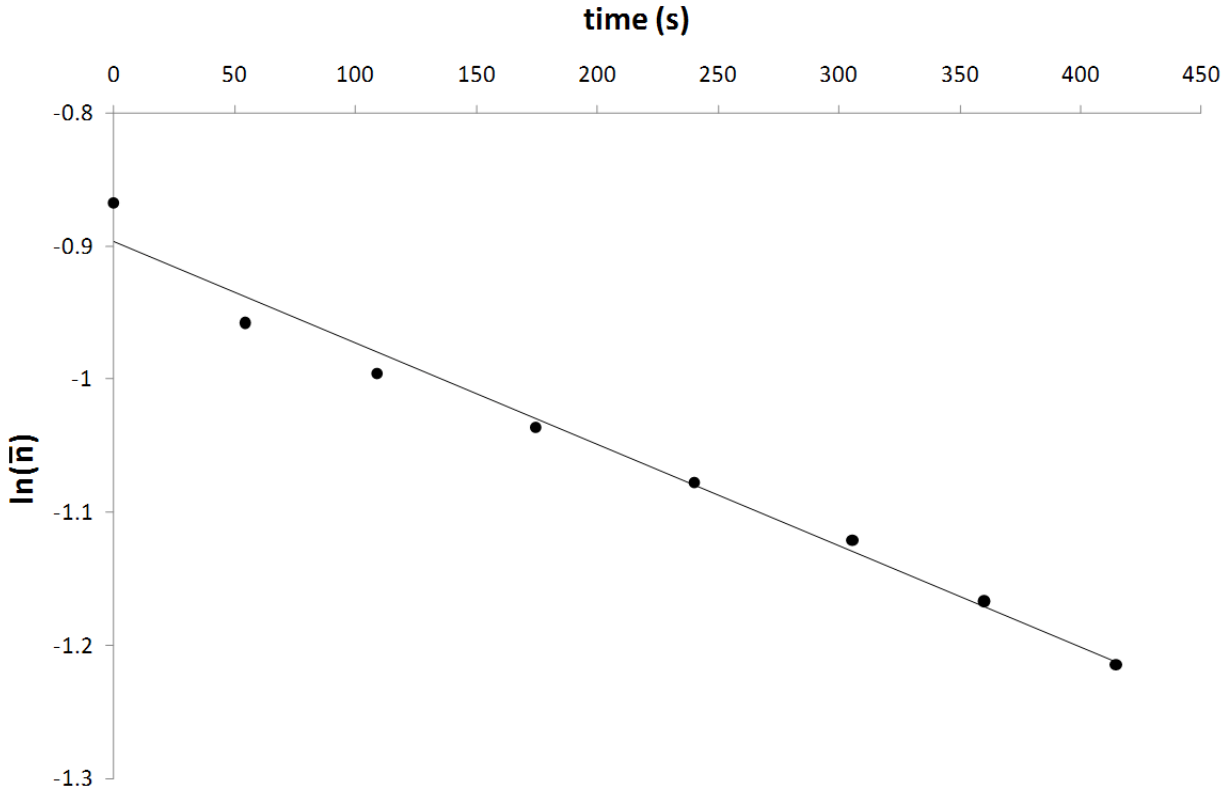

92-94 nm
0.000
-0.005
-0.010
-0.015
β_1
$k_{\text{continuous}}$
k_{exp}
k_{discrete}
0.0015
0.0025
β_0
79-81 nm
0.005
0.000
-0.005
-0.010
-0.015
β_1
$k_{\text{continuous}}$
k_{exp}
k_{discrete}
0.0015
0.0030
0.0045
β_0
44-45 nm
0.01
0.00
-0.01
-0.02
-0.03
-0.04
β_1
$k_{\text{continuous}}$
k_{exp}
k_{discrete}
0.006
0.008
0.010
β_0
25-26 nm
0.00
-0.05
-0.10
β_1
$k_{\text{continuous}}$
k_{exp}
k_{discrete}
0.016
0.020
0.024
β_0

Figure 4

(a)


0.45
0.4
0.35
0.3
0.25
0.2
n̄
0
100
200
300
400
500
600
700
800
900
time (s)

(b)


time (s)
0
50
100
150
200
250
300
350
400
450
-0.8
-0.9
-1
-1.1
-1.2
-1.3
ln(n̄)

(c)